J. Chem. & Cheml. Sci. Vol.1 (1), 75-78 (2010)

Perchloric Acid Initiated Polymerization of Acrylic Acid

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ABSTRACT

Chemical polymerization of acrylic acid at room temperature (~ 25^0c) was examined by using perchloric acid as an initiator in aqueous solvent. When the polymerization of acrylic acid was carried out with perchloric acid in H_2O a cross linked water-insoluble gel formation takes place. The polymer yield increases with an increase in concentration of the monomer and perchloric acid. Raising the reaction temperature also enhances the polymerization rate. The degree of swelling of gel polymer and adhesive nature of polyacrylic acid were also discussed.

Keywords: Perchloric acid ($HClO_4$), Chemical Polymerization, Acrylic acid (AA).

INTRODUCTION

The polymerization of acrylamide have been reported to take place in presence of HNO_3, $HClO_4$ in aqueous and organic solvent media[1,2]. The work has been extended to acrylic acid which the present article briefly describes. Polyacrylic acid is commercially useful and have wide applications in various field because polymer is found as a gel in different media.

EXPERIMENTAL PART

Meterials: Water was fractionally distilled three times. Organic solvents were also fractionally distilled to obtain pure samples. AA, $CHlO_4$ (70% pure) were of analytical grades and were used without further purification.

Polymerization: The reaction mixture containing AA with known amount of the $HClO_4$ as an initiator was taken into a glass vial which was tightly stoppered and thermostated. After measured period of time the polymerizing mixture was precipitated in a excess suitable solvent which was filtered off dried in vacuum and weighed. Considerable difficulty was usually encountered in extracting the polymer since it stuck as one solid mass in vial. On drying the rubber like gel polymer become hard and brittle, it had a glassy appearance and imbibed many times solvent by weight. Also it was insoluble in all the common solvents.

RESULTS AND DISCUSSION

We observed that when the polymerization of AA is initiated chemically with $HClO_4$ in H_2O, highly cross-lined

polymer was formed. The incidence of gelation was generally observed as the extent of conversion advanced beyond about 45% when the extent of polymer conversion is well below 45% viscous polymers predominate. The time dependence of the relative viscosity of the reaction mixture is followed by an abrupt increase in viscosity. This results from the occurrence of gelation. In the viscometer the reaction mixture was transformed into a glassy mass as was also observed in for HNO_3 and $HClO_4$ initiation with aqueous acrylamide solution[3].

Effect of concentration of AA:

An increase in the concentration of AA accelerates the process of gelation Table (I).

Effect of initiator concentration ($HClO_4$):

An increase in the concentration of $HClO_4$, the process of polymer formation increases Table (II).

Effect of temperature on polymerization:

Increasing the reaction temperature enhances the gel conversion as is illustrated in Table (III).

In each case there were found induction period which perhaps results from the presence of residual impurities in the reaction mixture.

These results are in accordance with those reported in literature[4,5] it appears that the intermolecular interaction of polymers initially formed with low molecular weights and being water-soluble may cause the gelation.

Degree of Swelling

The capacity of the resulting cross inked polymers to swell in various liquid was assessed by the degree of swelling, determined as the amount of liquid imbibed by unit mass of the polymers[6]. The pertinent results are presented in Table-IV. From this table it was observed that the degree of swelling of polyacrylic acid in different solvents are as:

$CH_3OH > C_2H_5OH >$ DMF > HCOOH > H_2O > Dioxane > CH_3COOH.

Also, the order of degree of swelling in binary miscible solvents [50-50% (v-v)] were observed after 24 hrs as:

$CH_3OH - C_2H_5OH > H_2O - C_2H_5OH > H_2O - CH_3COCH_3 > H_2O - CH_3COOH$.

Adhesive nature of PAA:

The adhesive properties of polyacrylic acid (PAA) was also observed. It was observed that polyacrylic acid and polymethacrylic acid are too water sensitive to serve as plastics[4,5]. They are brittle when dry and on heating do not become thermoplastic but cross-links char and decompose. In solution they show typical polyectrolyte behavior, including abnormally high viscosities. Because of this property they are useful as thickening agents for lattices and for adhesive. It was observed that polyacrylic acid was found to be extremely powerful adhesive. Adhesion occurs when the liquid polymer was spared or pasted in a thin layer between the surfaces to be bonded. This novel adhesive properties were tested with different materials were shown in the Table-V. Adhesion arises to part from mechanical interlocking between polymer and surface and in part from strong secondary bond forces.

Probable mechanism of polymerization:

The polymer formation with $HClO_4$ is completely inhibited by p-benzoquinone, opening the probable free radical polymerization mechanism.

In summary the present work demonstrates that $HClO_4$ acts as an initiator for acrylic acid polymerization. Further work on the quantitative aspects of kinetics, molecular weight determination and possible mechanism of polymerization is in progress.

Table – I
Aqueous Gel Polymerization of AA at its different concentration with $HClO_4$

[AA] Mole/*l*	Time of solid gel formation (days)	Color of Gel
0.70	80	Colorless
1.40	60	Colorless
28.80	40	Pale Yellow
5.60	15	Pale Brown

$HClO_4$ = 0.497 mole/*l*
Temperature, 40^0c

Table – II
Aqueous Gel Polymerization of AA with different concentrations of $HClO_4$

[$HClO_4$] Mole/*l*	Color of Gel	Time of gel formation (days)
0.144	Colorless	No gel formation
0.288	Viscous solution	30
0.497	Sold Brown gel	15
0.995	Solid Brown gel	12

[AA] = 5.60 mole/*l*
Temperature, 40^0C

Table – III
Aqueous Gel Polymerization of AA – at its different temperature with $HClO_4$

Temperature 0°C	Time of Solid gel formation (days)
25	60
40	15
60	40

* [AA] = 5.6 mole/*l*
** [$HClO_4$] = 0.497 mole/*l*

Table – IV
Degree of swelling of Gel Polyacrylic acid in pure and miscible solvents.

Pure solvent	Degree of swelling (∞)*	Binary miscible solvent (50-50)% (v-v)	Degree of Swelling (∞)*
(1) Ethanol	13.40	(1) Water – acetone	8.95
(2) Dioxane	05.16	(2) Water-ethanol	9.42
(3) DMF	13.10	(3) Acetone-chloroform	0.200
(4) Formic Acid	11.00	(4) Methanol-ethanol	16.00
(5)Glacial Acetic Acid	4.88	(5) Water-Glacial acetic acid	8.00
(6) Chloroform	0.40		
(7) Methanol	13.90		
(8) Glycerol	0.56		
(9) Water	8.90		
(10) Acetone	2.90		

* Degree of swelling was noted after 24 hrs.

Table – V
Adhesives nature of Gel Polyacrylic Acid with different materials.

Materials	Excellent	Poor	Non -Adhesives
1. Marble – Marble Stone	√	-	-
2. Paper – Paper	√	-	-
3. Rough Paper - Rough Paper	√	-	-
4. Rough Paper – Jute	√	-	-
5. Rough Paper – Cotton thread	√	-	-
6. Rough Paper – Rubber	√	-	-
7. Filter Paper – Filter Paper	-	√	-
8. Plywood – Plywood	-	√	-
9. Bamboo – Bamboo (Vertical)	√	-	-
10. Bamboo – Bamboo (Horizental)	√	-	-
11. Wood – Bamboo	√	-	-
12. Jute – Jute	-	-	√
13. Metal – Metal	-	-	√
14. Cotton thread – Cotton thread	-	-	√
15. Coin (Alloys) – News Paper	√	-	-
16. Plastic – Plastic	-	-	√
17. Glass – Plastic	-	-	√
18. Leather – Leather	√	-	-
19. Wool – Wool	-	-	√
20. Marble Power – Plane Paper	-	-	√

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